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TITLE: BATTERY CATHODE

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## BATTERY CATHODE

This application is a continuation-in-part of U.S. Serial No. 09/001,822, filed on December 31, 1997.

The present invention relates to batteries.

10 Batteries, such as alkaline batteries, are commonly  
used as energy sources. Generally, alkaline batteries have  
a cathode, an anode, a separator and an electrolytic  
solution. The cathode is typically formed of manganese  
dioxide, carbon particles and a binder. The anode can be  
15 formed of a gel including zinc particles. The separator is  
usually disposed between the cathode and the anode. The  
electrolytic solution, which is dispersed throughout the  
battery, can be a hydroxide solution.

20           The invention relates to batteries, such as alkaline  
batteries, having cathodes that include manganese dioxide  
and relatively small nonsynthetic, nonexpanded graphite  
particles. These batteries have good performance  
characteristics. For example, the batteries can exhibit  
25   high energy output at a high discharge rate, such as a  
discharge rate equal to at least the battery's capacity (in  
units of Ampere-hours) discharged in one hour. The  
batteries can have various industry standard sizes, such as  
AA, AAA, AAAA, C or D.

30 "Nonsynthetic graphite particles" refer to graphite particles that are prepared without using an industrial or laboratory graphitization process.

"Nonexpanded graphite particles" refer to graphite particles that are prepared without any industrial or laboratory particle expansion process.

In one aspect, the invention features a cathode that includes manganese dioxide and nonsynthetic, nonexpanded graphite particles having an average particle size of less than about 20 microns.

5       The particle size is measured using a Sympatec HELIOS analyzer. For a given sample of graphite particles, the average particle size is the particle size for which half the volume of the sample has a smaller particle size.

10       In another aspect, the invention features an electrochemical cell including a cathode, an anode and a separator disposed between the cathode and the anode. The cathode includes manganese dioxide and nonsynthetic, nonexpanded graphite particles having an average particle size of less than about 20 microns.

15       In some embodiments, the separator includes a nonwoven, non-membrane material and a second nonwoven, non-membrane material disposed along a surface of the first material. In these embodiments, the separator can be devoid of a membrane layer or an adhesive layer disposed between  
20       the nonwoven, non-membrane materials. A membrane material refers to a material having an average pore size of less than about 0.5 micron, whereas a non-membrane material refers to a material having an average pore size of at least about 5 microns.

25       The cathode can have a porosity of from about 21% to about 28%. The porosity of the cathode is the relative volume of the cathode that is not taken up by solid material, such as, for example, manganese dioxide, graphite particles and binder.

30       The anode can have a porosity of from about 2 grams of zinc particles to about 2.45 grams of zinc particles per cubic centimeter of anode volume that is taken up by liquid or solid material.

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20 The amount of graphite particles disposed within  
cathode 12 should be enough to improve the overall  
conductivity of cathode 12 while having minimal impact on  
the energy capacity of battery 10. Preferably, cathode 12  
is from about 4 weight percent to about 10 weight percent  
25 graphite particles, more preferably from about 5 weight  
percent to about 9 weight percent graphite particles, and  
most preferably from about 6 weight percent to about 8  
weight percent graphite particles. These weight percentage  
ranges correspond to when the electrolytic solution is not  
30 dispersed within cathode 12.

Cathode 12 can be a single pellet of material. Alternatively, cathode 12 can be formed of a number of cathode pellets that are stacked on top of each other. In

either case, the cathode pellets can be made by first mixing the manganese dioxide, graphite particles and optionally the binder. For embodiments in which more than one pellet is used, the mixture can be pressed to form the pellets. The  
5 pellet(s) are fit within battery 10 using standard processes. For example, in one process, a core rod is placed in the central cavity of battery 10, and a punch is then used to pressurize the top most pellet. When using  
10 this process, the interior of wall 18 can have one or more vertical ridges that are spaced circumferentially around wall 18. These ridges can assist in holding cathode 12 in place within battery 10.

In embodiments in which cathode 12 is formed of a single pellet, the powder can be placed directly within  
15 battery 10. A retaining ring is set in place, and an extrusion rod passes through the ring, densifying the powder and forming cathode 12.

In certain embodiments, a layer of conductive material can be disposed between wall 18 and cathode 12.  
20 This layer may be disposed along the inner surface of wall 18, along the outer circumference of cathode 12 or both. Typically, this conductive layer is formed of a carbonaceous material. Such materials include LB1000 (Timcal), Eccocoat 257 (W.R. Grace & Co.), Electrodag 109 (Acheson Industries,  
25 Inc.), Electrodag 112 (Acheson) and EB005 (Acheson). Methods of applying the conductive layer are disclosed in, for example, Canadian Patent No. 1,263,697, which is hereby incorporated by reference.

Using a conductive layer, especially Electrodag 109  
30 or EB005, between wall 18 and cathode 12 can reduce the pressure used when forming cathode 12 within battery 10. Thus, the porosity of cathode 12 can be made relatively high without causing the pellet(s) to be crushed or crack when



forming cathode 12 within battery 10. However, if the porosity of cathode 12 is too low, an insufficient amount of electrolytic solution can be dispersed within cathode 12, reducing the efficiency of battery 10. Thus, in certain  
5 embodiments, cathode 12 has a porosity of from about 21% to about 28%, more preferably from about 25% to about 27%, and most preferably about 26%.

Within cathode 12, any of the conventional forms of manganese dioxide for batteries can be used. Distributors  
10 of such manganese dioxide include Kerr McGee, Co., Broken Hill Proprietary, Chem Metals, Co., Tosoh, Delta Manganese, Mitsui Chemicals and JMC.

In certain embodiments, cathode 12 can have from about 8.9 grams of manganese dioxide to about 9.8 grams of  
15 manganese dioxide. In these embodiments, cathode 12 preferably includes from about 9.3 grams to about 9.8 grams of manganese dioxide, more preferably from about 9.4 grams to about 9.65 grams of manganese dioxide, and most preferably from about 9.45 grams of manganese dioxide to  
20 about 9.6 grams of manganese dioxide.

In other embodiments, cathode 12 preferably includes from about 4 grams to about 4.3 grams of manganese dioxide, more preferably from about 4.05 grams to about 4.25 grams of  
25 manganese dioxide, and most preferably from about 4.1 grams to about 4.2 grams of manganese dioxide.

In some embodiments, cathode 12 may further include a binder. Examples of binders for cathode 12 include polyethylene powders, polyacrylamides, Portland cement and fluorocarbon resins, such as PVDF and PTFE. In certain  
30 embodiments, cathode 12 includes a polyethylene binder sold under the tradename coathylene HA-1681 (Hoescht). When cathode 12 includes a binder, the binder preferably makes up less than about 1 weight percent of cathode 12, more

5 cathode 12.

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


5 about 1.75 grams of zinc particles.

10 from about 68 weight percent to about 72 weight percent zinc particles. These weight percentages correspond to when the electrolytic solution is dispersed within anode 14.

15 salts of polyacrylic acids, carboxymethylcellulose or combinations thereof. Examples of such polyacrylic acids are Carbopol 940 (B.F. Goodrich) and Polygel 4P(3V), and an example of a grafted starch material is Waterlock A221 (Grain Processing Corporation, Muscatine, IA). An example  
20 of a salt of a polyacrylic acid is CL15 (Allied Colloids). In some embodiments, anode 14 preferably includes from about 0.2 weight percent to about 1 weight percent total gelling agent, more preferably from about 0.4 weight percent to about 0.7 weight percent total gelling agent, and most  
25 preferably from about 0.5 weight percent to about 0.6 weight percent total gelling agent. These weight percentages correspond to when the electrolytic solution is dispersed within anode 14.

30 as bismuth, tin, lead and indium. Alternatively, gassing inhibitors can be organic compounds, such as phosphate esters, ionic surfactants or nonionic surfactants. Examples of ionic surfactants are disclosed in, for example, U.S.



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embodiments, the electrolytic solution is an aqueous solution of potassium hydroxide including from about 33 weight percent to about 38 weight percent potassium hydroxide.

5 In certain embodiments, battery 10 preferably includes from about 3.4 grams to about 3.9 grams of electrolytic solution, more preferably from about 3.45 grams to about 3.65 grams of electrolytic solution, and most preferably from about 3.5 grams to about 3.6 grams of  
10 electrolytic solution.

In other embodiments, battery 10 preferably includes from about 1.6 grams to about 1.9 grams of electrolytic solution, more preferably from about 1.65 grams to about 1.85 grams of electrolytic solution, and most preferably from about 1.7 grams to about 1.8 grams of electrolytic solution.

The weight ratio of manganese dioxide to electrolytic solution can be from about 2.2 to about 2.9, and the weight ratio of zinc particles to electrolytic solution can be from about 0.9 to about 1.25. In some embodiments, the weight ratio of manganese dioxide to electrolytic solution is from about 2.5 to about 2.9, and the weight ratio of zinc particles to electrolytic solution is from about 1.1 to about 1.25. In other embodiments, the weight ratio of manganese dioxide to electrolytic solution is from about 2.5 to about 2.65, and the weight ratio of zinc particles to electrolytic solution is from about 0.9 to about 1.2. These weight ratios are based on the amount of electrolytic solution dispersed throughout the anode, cathode and separator.

The batteries can be AA or AAA batteries that demonstrate good results when tested according to the cc photo test, the 1 Watt continuous test, the half Watt

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Battery 10 can be a AA battery that offers excellent performance according to the half Watt rm test (described below). For example, when discharged to 1.1 Volts according to the half Watt rm test, the AA battery can give at least about 1.5 hours, at least about 2 hours, at least about 2.5 hours or at least about 2.65 hours. When discharged to 0.9 Volts according to the half Watt rm test, the AA battery can give at least 2.9 hours, at least about 3 hours, at least about 3.25 hours or at least about 3.4 hours.

10 Battery 10 can be a AAA battery that offers excellent performance according to the half Watt continuous test (described below). For example, when discharged to 1 Volt according to the half Watt continuous test, the AAA battery can give at least about 0.65 hours, at least about 15 0.7 hours, at least about 0.75 hours or at least about 0.8 hours. When discharged to 0.9 Volts according to the half Watt continuous test, the AAA battery can give at least 0.9 hours, at least about 0.95 hours, at least about 1. hour or at least about 1.05 hours.

20 Battery 10 can be a AAA battery that offers excellent performance according to the pulsed test (described below). For example, when discharged to 1 Volt according to the pulsed test, the AAA battery can give at least about 0.35 hours, at least about 0.4 hours, at least 25 about 0.45 hours or at least about 0.5 hours. When discharged to 0.9 Volts according to the pulsed test, the AAA battery can give at least 0.65 hours, at least about 0.7 hours, at least about 0.75 hours or at least about 0.8 hours.

30 Battery 10 can be a AAA battery that offers excellent performance according to the half Watt rm test (described below). For example, when discharged to 1.1 Volts according to the half Watt rm test, the AAA battery

Battery 10 can be a AAA battery that offers excellent performance according to the quarter Watt rm test (described below). For example, when discharged to 1.1 Volts according to the quarter Watt rm test, the AAA battery can give at least about 2 hours, at least about 2.1 hours, at least about 2.2 hours or at least about 2.3 hours. When discharged to 0.9 Volts according to the quarter Watt rm test, the AAA battery can give at least 3.1 hours, at least about 3.25 hours, at least about 3.4 hours or at least about 3.5 hours.

AA batteries were prepared with the following components. The cathode included about 9.487 grams of manganese dioxide (Kerr-McGee, Co.), about 0.806 grams of nonsynthetic, nonexpanded graphite having an average particle size of about 7 microns (Brazilian Nacional de Grafite) and about 0.3 weight percent of coathylene HA-1681. The anode included about 3.976 grams of zinc particles, about 50 ppm surfactant (RM510, Rhone Poulenc) relative to zinc, and about 0.5 weight percent total gelling agent (Carbopol 940 and A221). The porosity of the cathode was about 26%, and the porosity of the anode was about 2.173 grams of zinc per cubic centimeter of anode. The separator was a two-layer structure with each layer formed of a nonwoven material including about 57 weight percent PVA fibers (about 0.5 denier at 6 millimeters), about 30 weight percent rayon fibers (about 1.5 denier at 6 millimeters) and



about 13 weight percent PVA binder. Each layer was about 5.4 mils thick when dry and about 10 mils thick when wet. Each layer had a basis weight of about 54 grams per square meter. The separator did not include an adhesive, and the  
5 layers were substantially devoid of any filler. The battery also included about 3.598 grams of an aqueous potassium hydroxide (about 35.5 weight percent potassium hydroxide) solution. A thin coating of EB005 (Acheson) was disposed between the outer wall of the battery and the outer  
10 periphery of the cathode.

The AA batteries were stored at a temperature of from about 20.1°C to about 22.1°C for five days. The AA batteries were then stored according to the following procedure.

15 Each battery is visually examined for leakage or material damage and identified such that battery identification can be maintained throughout the test program. The batteries are oriented on their sides in holding trays such that the batteries are not in physical  
20 contact with each other. The holding trays are made to be resistant to heat and electrolytes. The trays are stored for 1 day at ambient conditions, after which the trays are placed into a preheated chamber. The trays are spaced so that there is at least about 5 cm (2 inches) of space  
25 between the chamber wall, and the tray above, below, or adjacent to each tray. The following 24 hour test sequence, shown in Table I, is repeated for 14 days.

Table I

Cycle Number	Time (Hrs.)	Temperature ( $\pm 2^{\circ}\text{C}$ )
1	6.0	Ramp from 28 to 25
2	4.5	Ramp from 25 to 34
3	2.0	Ramp from 34 to 43
4	1.0	Ramp from 43 to 48
5	1.0	Ramp from 48 to 55
6	1.0	Ramp from 55 to 48
7	1.0	Ramp from 48 to 43
8	3.0	Ramp from 43 to 32
9	<u>4.5</u> 24.0 (1 Day)	Ramp from 32 to 28

The trays are removed from the chamber and each battery is visually examined for leakage or material damage.

The following tests were subsequently performed on individual AA batteries. Each test was conducted at a temperature of from about 20.1°C to about 22.1°C.

A AA battery was discharged from an open circuit voltage of about 1.6 Volts under constant current conditions of ten seconds per minute for one hour per day ("the cc photo test"). The AA battery reached 1 Volt after 203 pulses, and the AA battery reached 0.8 Volts after 443 pulses.

A AA battery was continuously discharged from an open circuit voltage of about 1.6 Volts at 1 Watt ("the 1 Watt continuous test"). The AA battery reached 1 Volt after about 0.75 hours, and the AA battery reached 0.8 Volts after about 1.00 hours.

A AA battery was continuously discharged from an open circuit voltage of about 1.6 Volts at a rate that

alternated between 1 Watt (3 second pulses) and 0.1 Watt (7 second pulses) ("the pulsed test"). The AA battery reached 1 Volt after about 2.16 hours, and the AA battery reached 0.8 Volts after about 3.72 hours.

5 A AA battery was discharged from an open circuit voltage of about 1.6 Volts at 0.5 Watts for 15 minutes per hour ("the half Watt rm test"). The AA battery reached 1.1 Volts after about 1.87 hours, and the AA battery reached 0.9 Volts after about 3.34 hours.

10 Example II

A AAA battery was prepared. The cathode 12 included about 4.155 grams of manganese dioxide (Kerr McGee, Co.), about 0.353 grams of nonsynthetic, nonexpanded graphite having an average particle size of about 7 microns (Brazilian Nacional de Grafite) and about 0.3 weight percent of coathylene HA-1681. The anode 14 included about 1.668 grams of zinc particles and about 0.5 weight percent total gelling agent (Carbopol 940 and A221). The porosity of the cathode was about 26%, and the porosity of the anode was about 2.266 grams of zinc per cubic centimeter of anode 14. The separator included two layers of nonwoven material. The separator was a two-layer structure with each layer formed of a nonwoven material including about 57 weight percent PVA binders (about 0.5 denier at 6 millimeters), about 30 weight percent cellulose fibers (about 1.5 denier at 6 millimeters) and about 13 weight percent PVA binder. Each layer was about 5.4 millimeters thick when dry and about 10 millimeters thick when wet. Each layer had a basis weight of about 54 grams per square meter. The separator did not include an adhesive, and the layers were substantially devoid of any filler. The battery also included about 1.72 grams of an aqueous potassium hydroxide (about 35.5 weight percent) solution. A thin coating of EB005 was disposed

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With the half Watt rm test, a AAA battery took about 0.57 hours to reach 1 Volt, and about 1.08 hours to reach 0.8 Volts.

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### Example III

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1.66 hours, and the AA battery reached 0.9 volts after about 3.05 hours.

Other embodiments are within the claims.

What is claimed is: